RC-P04

Cleaning of Silicon-Containing Carbon Contamination

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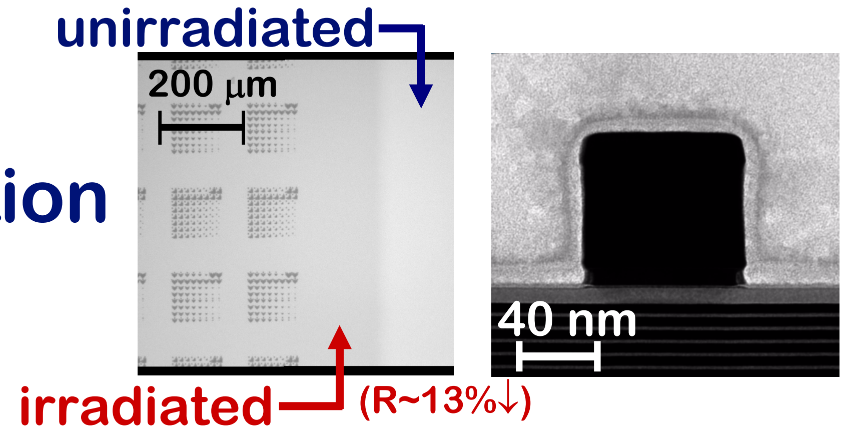
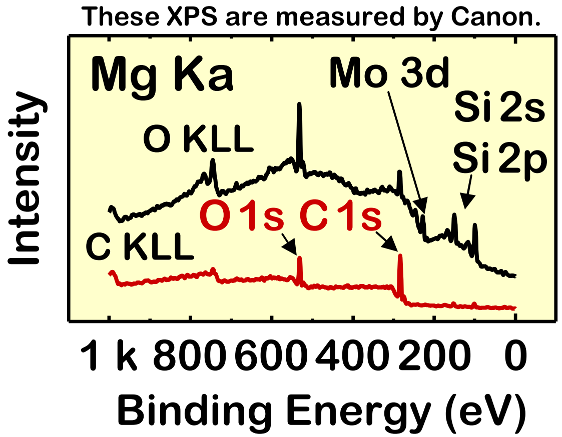
Contamination and Cleaning

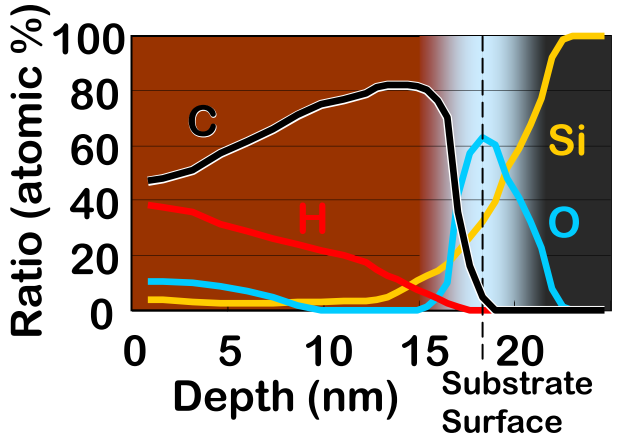
- EUV masks and mirrors are contaminated by EUV irradiation in an usual vacuum condition.



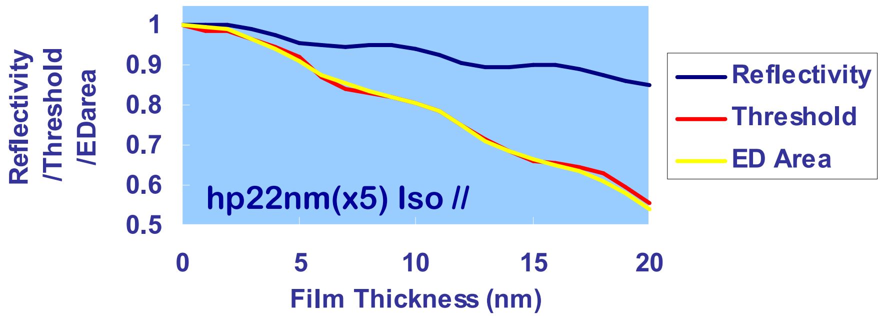
- Contamination mainly consists of carbon and hydrogen.

These XPS are measured by Canon.





- Contamination deteriorates lithographic performance.
$\rightarrow$ It must be cleaned.

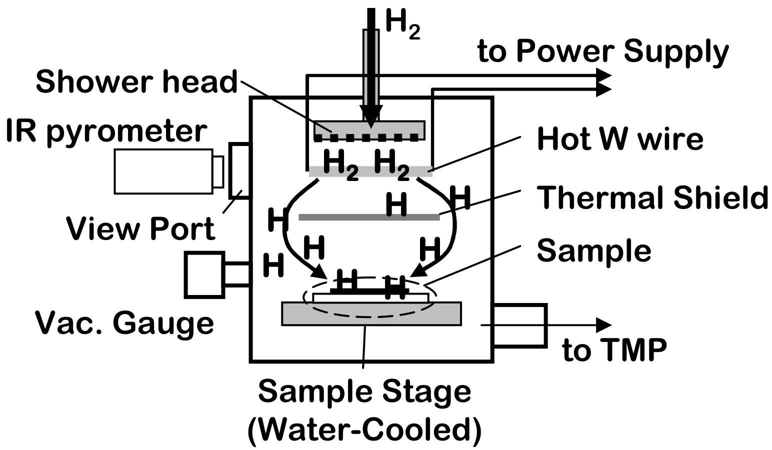


Reported Cleaning Studies

Technique	Rate	Advanttages Problems	Institution [Reference]
Oxygen Plasma Hydrogen Plasma	<0.1 nm/min	•Low speed •Reflectivity down	SNL [SPIE,4688,431(2002)]
EUV + O_2	0.24 nm/min	•Easy to apply •Low speed	LASTI [MNC2003]
UV/O_3	~1 nm/min	•readily available •Difficulty in UV Irradiation	LASTI [JVSTB, 23, 247 (2005)]
Hydrogen Radical (Hot Filament)	~1 nm/min	•Recovery from Ru oxidation •Heat load	ASET-Kyutech [JJAP, 46, L633 (2007)] Selete-Kyutech [EIPBN2008]
Shielded Plasma	5 nm/min	•Modest speed •Sputter damage	TNO [EUVL Symp. 2008]
	0.19 nm/min	•Damageless •Low speed	TNO [EUVL Symp. 2009]
Pure O_3	90 nm/min	•Extremely high speed	Selete-MEIDENSHA [EUVL Symp. 2009]

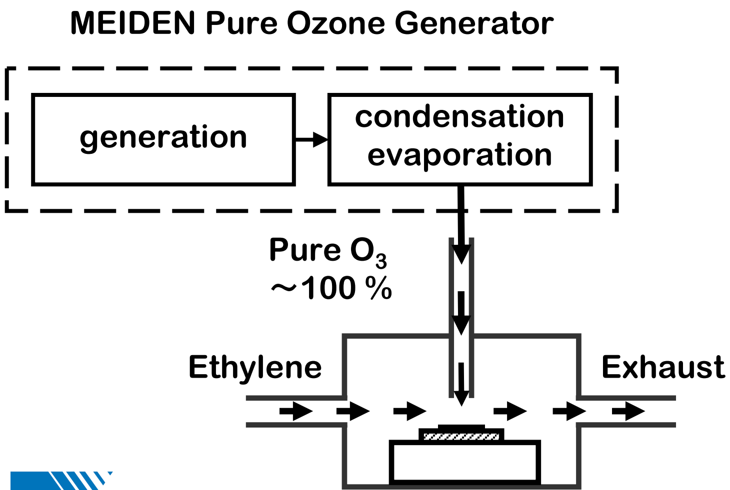
Our Previous Studies

● Hydrogen radical cleaning



- Simple hot W filament efficiently decomposes hydrogen molecule to hydrogen radical.
- Not only carbon contamination but also oxidation of Ru-capping layer can be recovered.
- Carbon removal rate ~ 1 nm/min.

● Pure ozone cleaning (alkene-gas assisted)

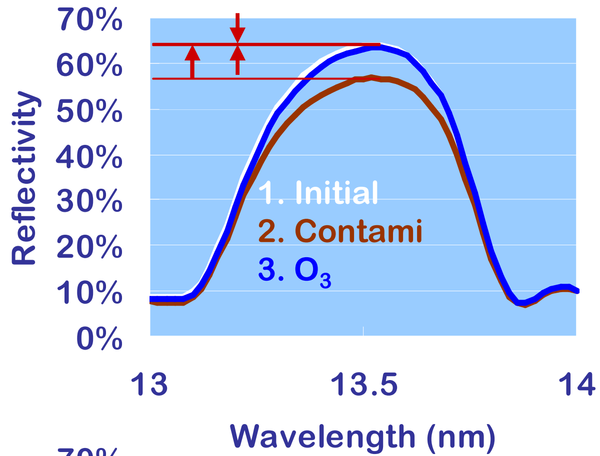


- Pure ozone is activated by the alkene assist gas.
- It needs no heating nor irradiation of any light (UV or EUV, etc.) and the removal rate is extremely high.
- Carbon removal rate ~ 90 nm/min.

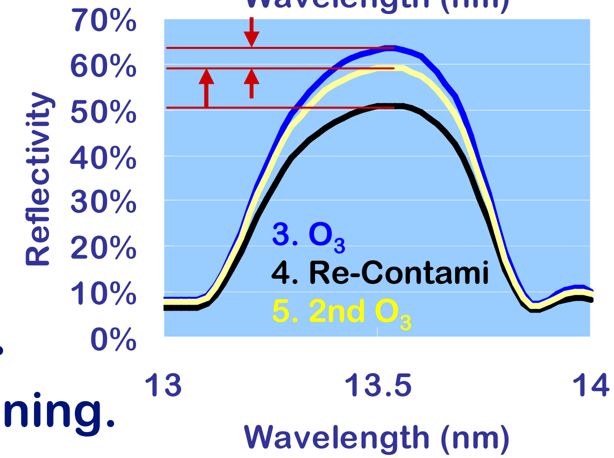
Problem Caused by Contained Si

- Using the pure O_3 cleaning, the reflectivity degradation of SR* contaminated multilayer mask brank is almost recovered.

  *Synchrotron Radiation



- However, the reflectivity recovery of strongly contaminated or multiple contaminated sample is not good enough.



- We investigated the cleaning residue.

  Note that Si capping layer is stable to pure O_3 cleaning.

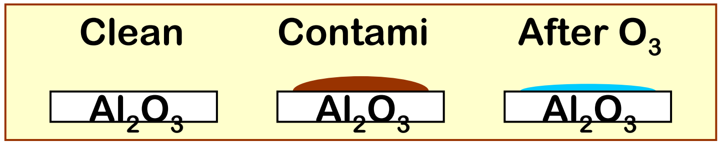
- The cause of accumulating degradation is **cleaning residue SiO_2.**

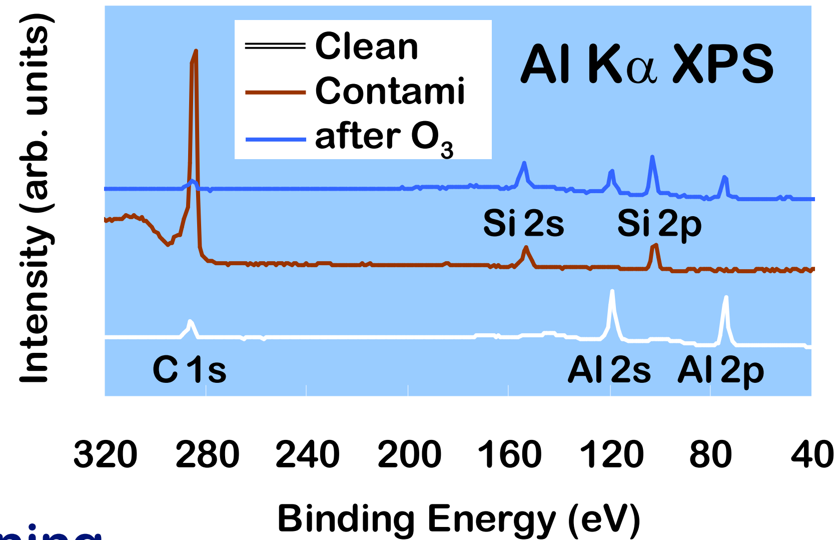
Chemical states of surface Si (XPS)

Atomic %	SiO_2	SiOx	Si^0
After 1st cleaning	38	4	58
After 2nd cleaning	73	0	27

Where Does Si Come from ?

- Almost all carboneous contamination we investigated (SR, DPP, LPP) contains several parcents of Si species.
  - Other groups also reported Si in contaminations.
  - Intel MET
    N1 mirror: C : O : Si ~70 % : 20 % : 10 %
    G1, G2 mirror: C : O : Si ~ 85 % : 10 % : 5 %
    Manish Chandhok, IEUVI Optics Contamination / Lifetime TWG (1st Mar. 2007)
  - Albany MET
    G2: C : O : Si : P : N = 74 : 20 : 2 : 2 : 1
    Andrea Wüest et al., IEUVI Optics Contamination / Lifetime TWG (1st Nov. 2007)
- The origin of Si was unclear. No Si species has been detected by QMS or GC-M.
  - So we deposited contamination on sapphier (Al_2O_3) substrates.





- The result clearly shows that **Si comes from vacuum.**
  In addition, this Si species seem hard to remove by oxidative cleaning.

Cleanablity Studies of Si:C

- **Experimental flow:**

  Si doped C (Si:C) sputter-deposited film → Characterization

  ↓

  Cleaning processing (Pure O_3, H-radical)

  ↓

  Characterization (XPS, HFS/RBS)

XPS: Xray Photoelectron Spectroscopy
HFS: Hydrogen Forward Schattering spectrometry
RBS: Rutherford Back Scattering spectrometry

- **Cleaning process condition:**

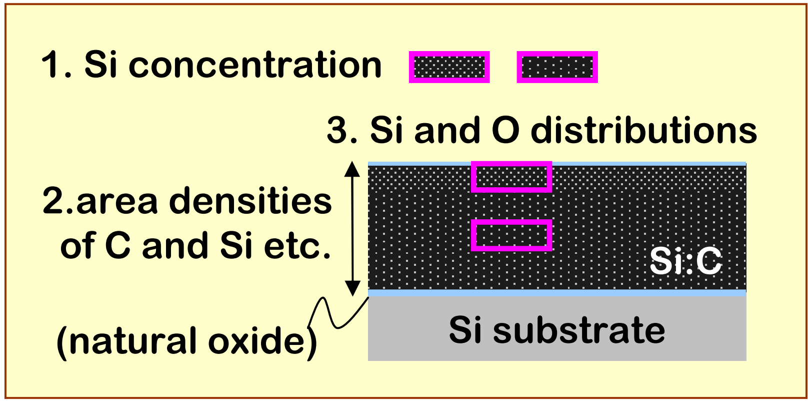
  Pure O_3 — assist gas = ethylene ~100 Pa
  room temperature

  H radical — gas pressure ~10^{-2} Pa
  filament temperature ~1780 °C

- **Characterization:**

  Si concentration dependence of film removal rate.

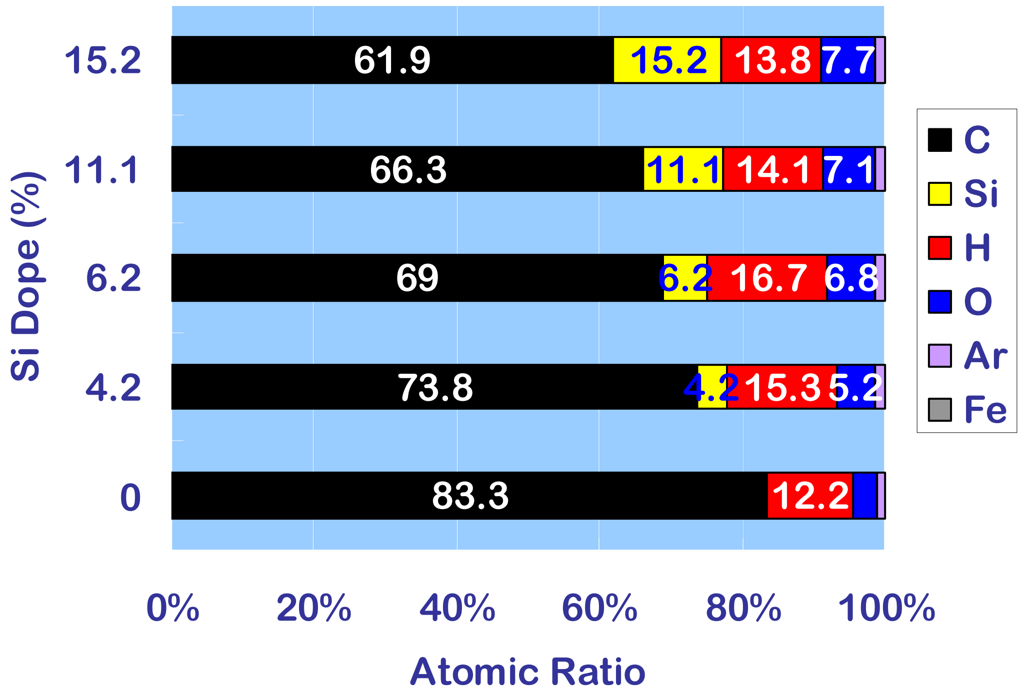
  Process time dependence of Si distribution.



Sample Characterization of Si:C

- C and Si are co-sputter-deposited on Si wafers.
  Doping rate is controlled by area of Si pieces placed on C target.

- RBS/HFS



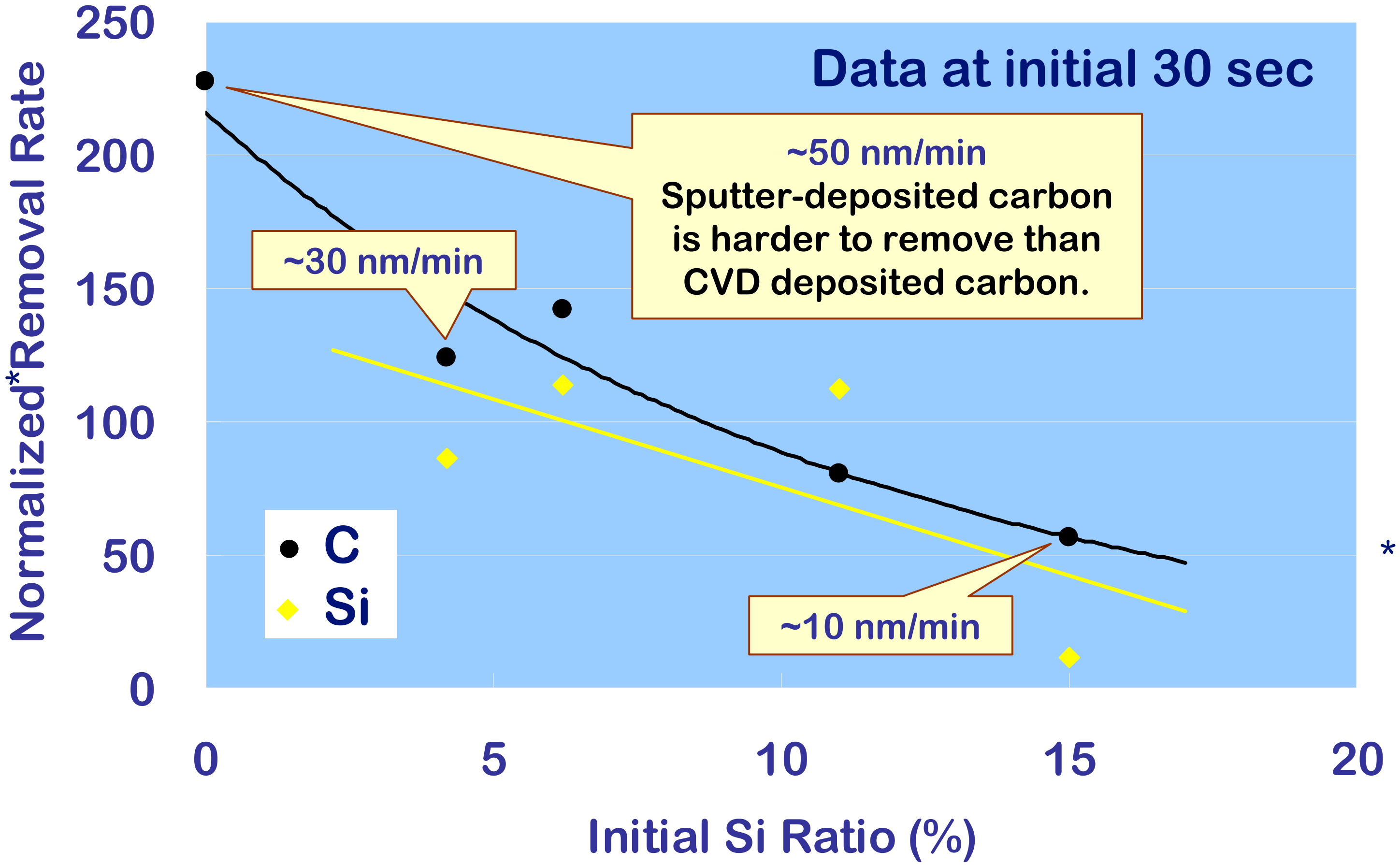
Si	Initial Area Density (10^{15}atom/cm^2)	Film Thickness (nm)
0 %	1435	146
4.2 %	1607	161
6.2 %	1532	153
11.1 %	1361	138
15.2 %	1282	128

- Converted from area density with bulk densities:
  C (amorphous) = 9.02~10.53×10^{22} atoms/cm^3
  SiO_2 (amorphous) = 6.62×10^{22} atoms/cm^3
  Si = 5.00×10^{22} atoms/cm^3

- XPS
  - ~70 % of C is C-C or C-H; π-π^* satellite is also observed.
  - Si mainly exists as SiOx (x<2); Si-C is not observed.

Si-Ratio Dependence for Pure O_3

RBS Result

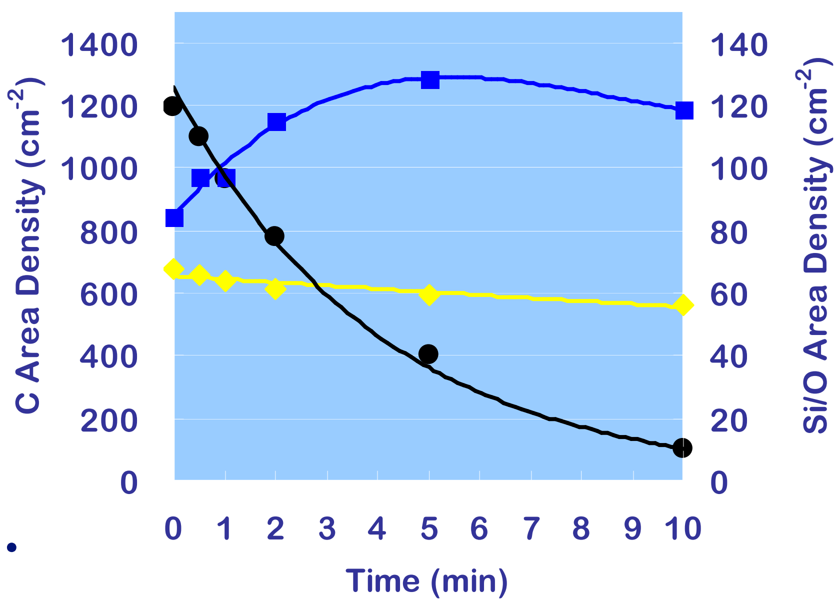


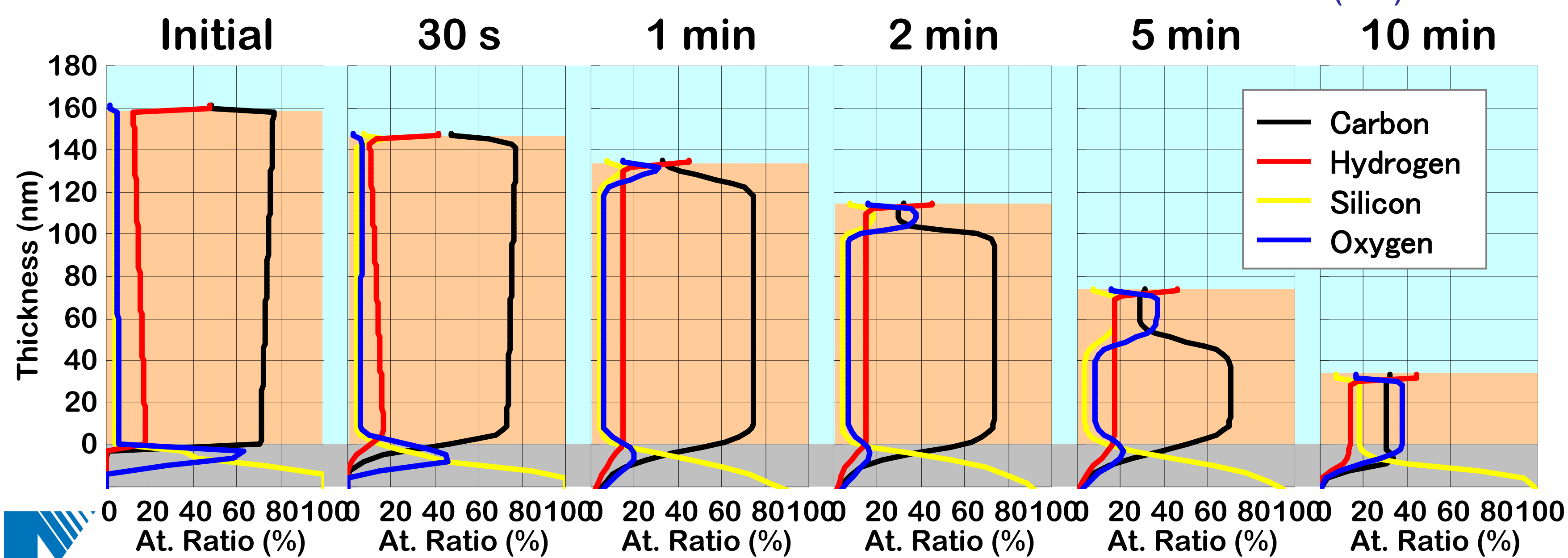
*Decresed amount par time par ratio of element

- Contained Si is also removed at initial stage.
- C removal rate decreses with Si concentration.

Change by Processing Time of Pure O_3

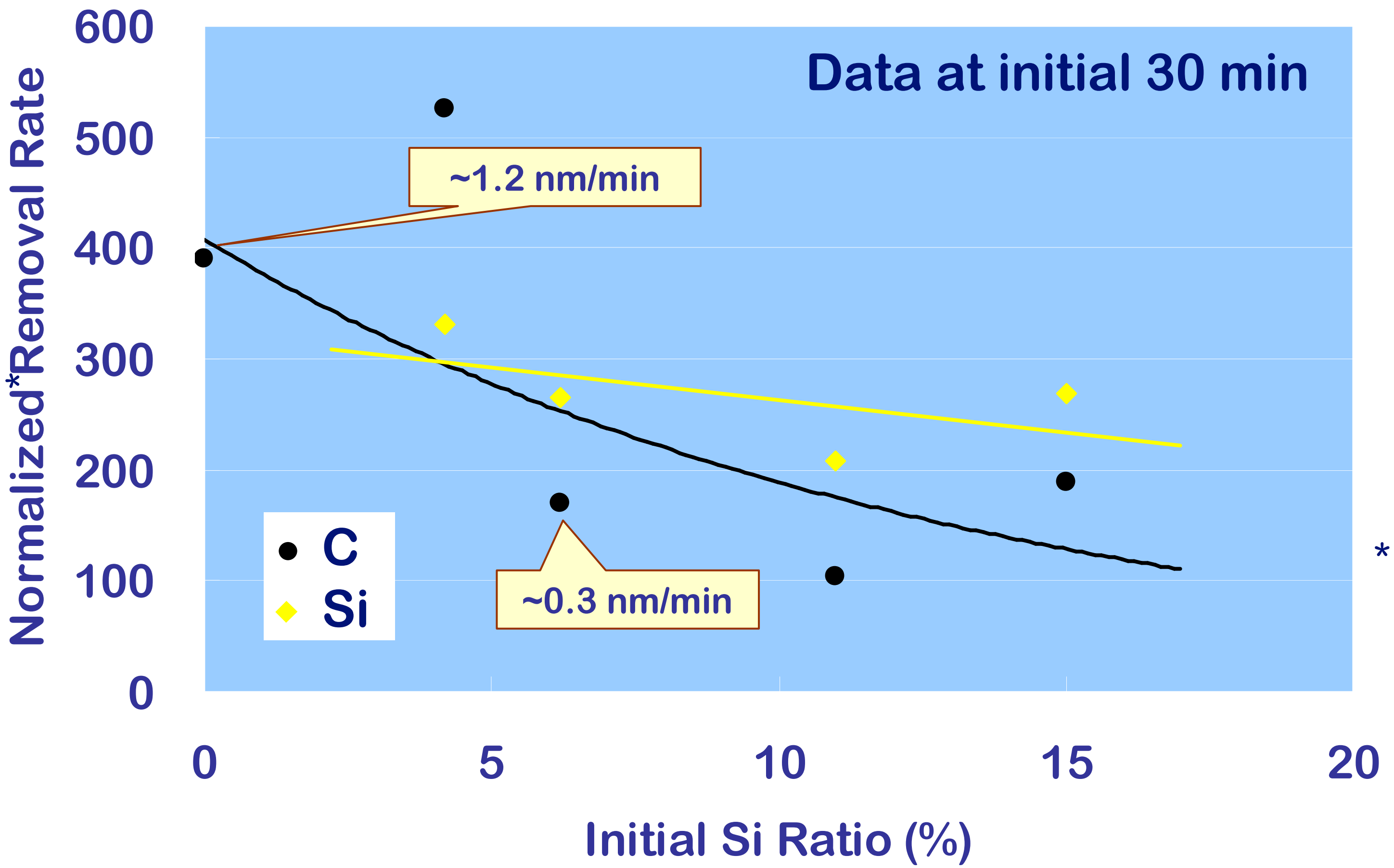
- We observed time dependence of depth profile of Si 4.2 % sample.
- C decreses with time but removal rate gradually slow down.
- Si also decreses but forms condensed layer at surface region.
- O increases and final ratio Si:O=1:2.





Si-Ratio Dependence for H-radical

RBS Result

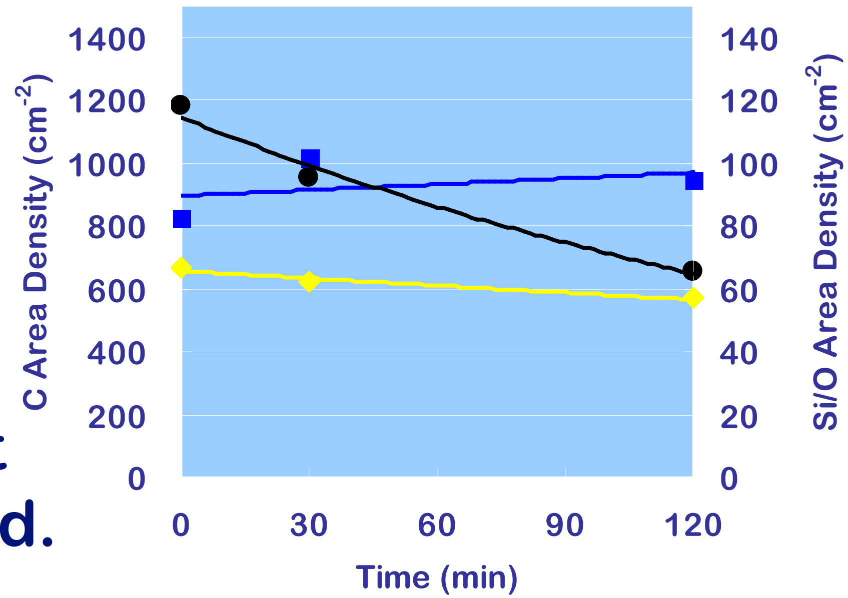


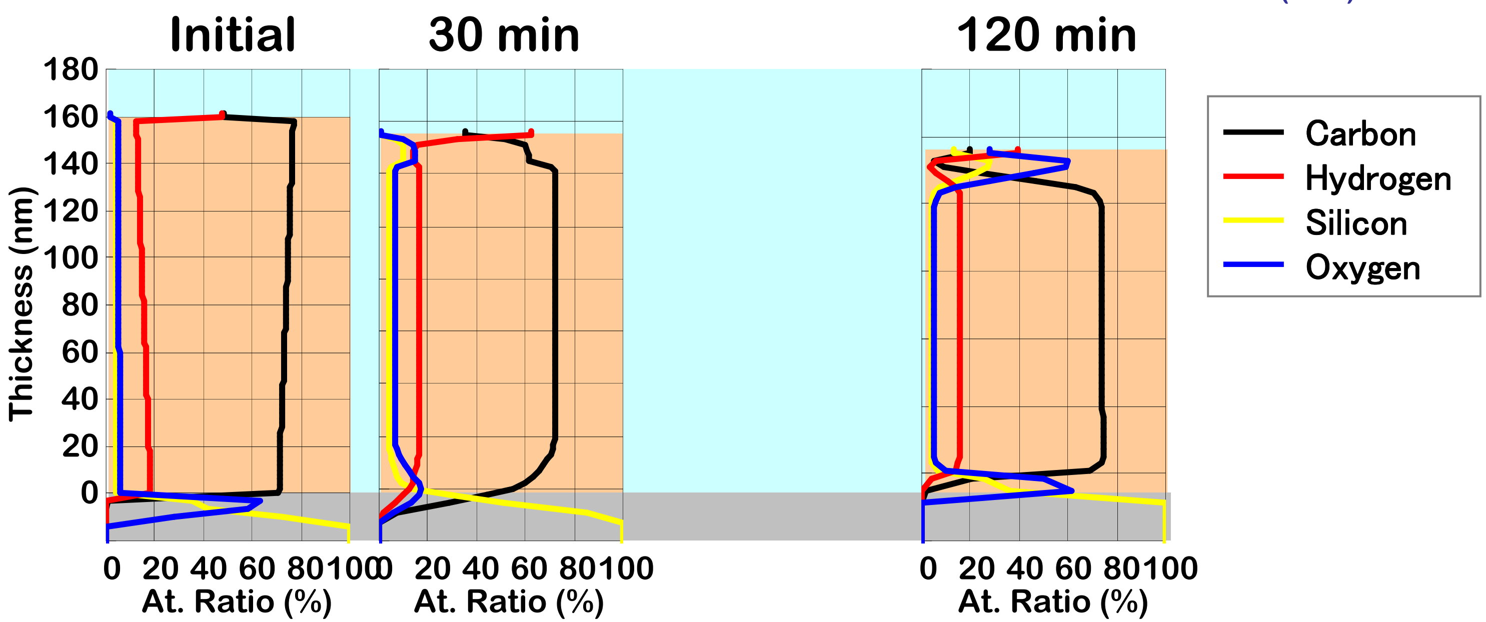
*Decresed amount par time par ratio of element

- Rate decrease with Si seems smaller than O_3.
- Si removal rate seems higher than O_3.

Change by Processing Time of H-radical

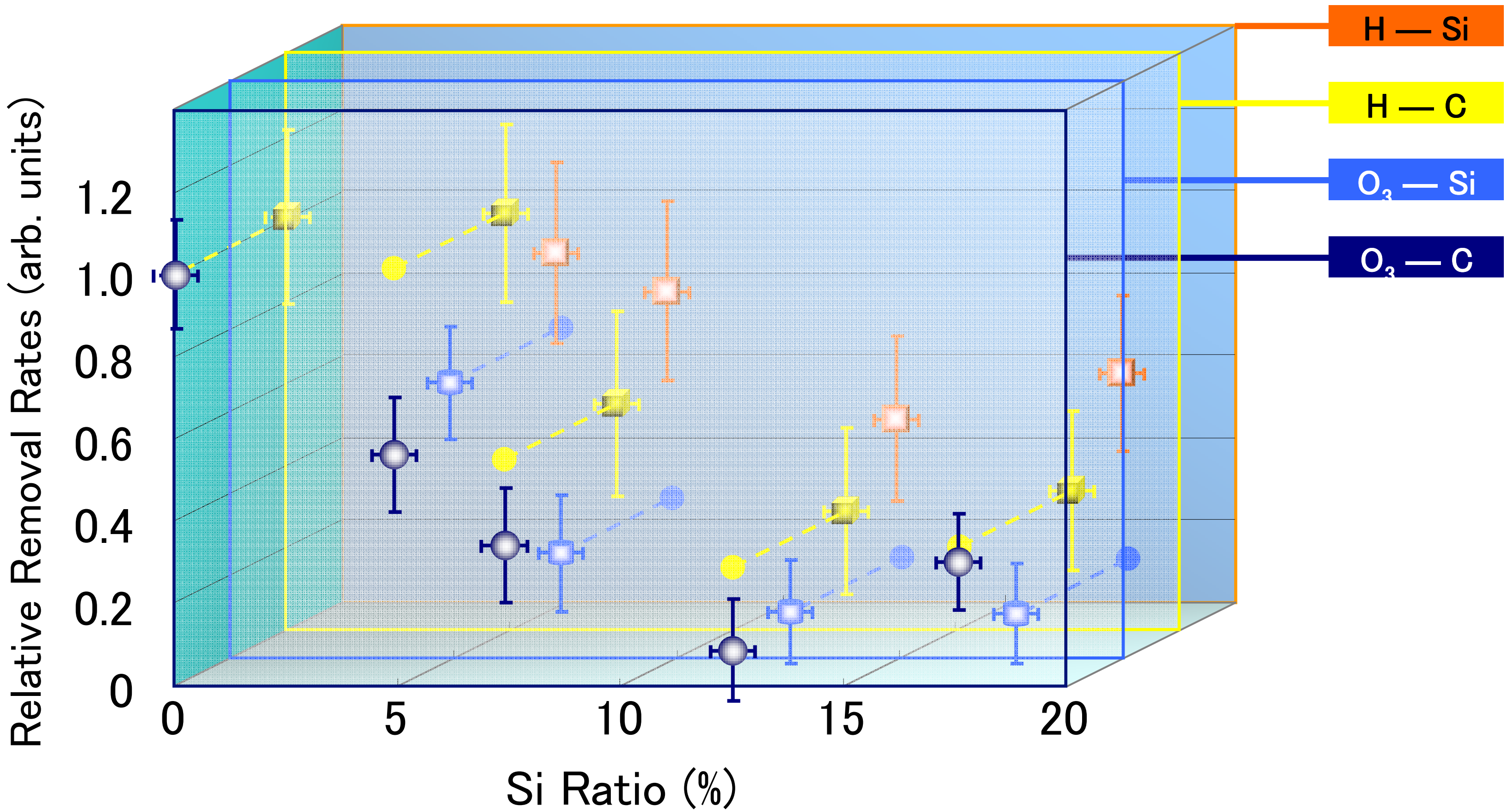
- We observed time dependence of depth profile of Si 4.2 % sample.
- 120 min H-radical processing seems correspond to 2~3 min prosessing of pure O_3.
- Si decreses faster than pure O_3 but SiO_2 condensed layer is also formed.





Comparison between H and Pure O_3

- Both of techniques removes a little Si but SiO_2 layers are formed at surface region.
- Absolute removal rate is several tens faster for pure O_3.
- Rate decrease by Si containing is smaller for H-radical.



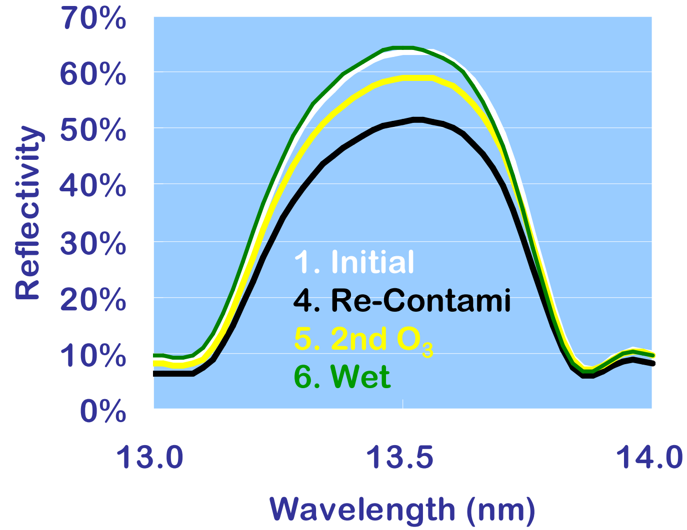
Recovery from SiO_2 Formation

- Once SiO_2 is formed, it seems hard to remove it by mild-dry process. Thus we tried wet etching.

Chemical states of surface Si (XPS)

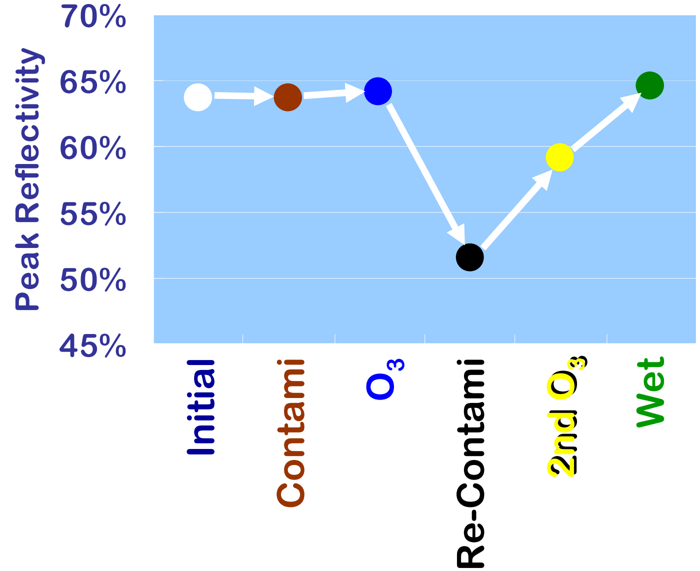
Atomic %	SiO_2	SiOx	Si^0	SiO_2 (nm)
After 1st cleaning	38	4	58	
After 2nd cleaning	73	0	27	3.8
After wet etching	29	0	71	1.1

Si^0 is Si in capping layer.



- Using wet etching process, SiO_2 residue has successfully removed and reflectivity was completely recoverd.

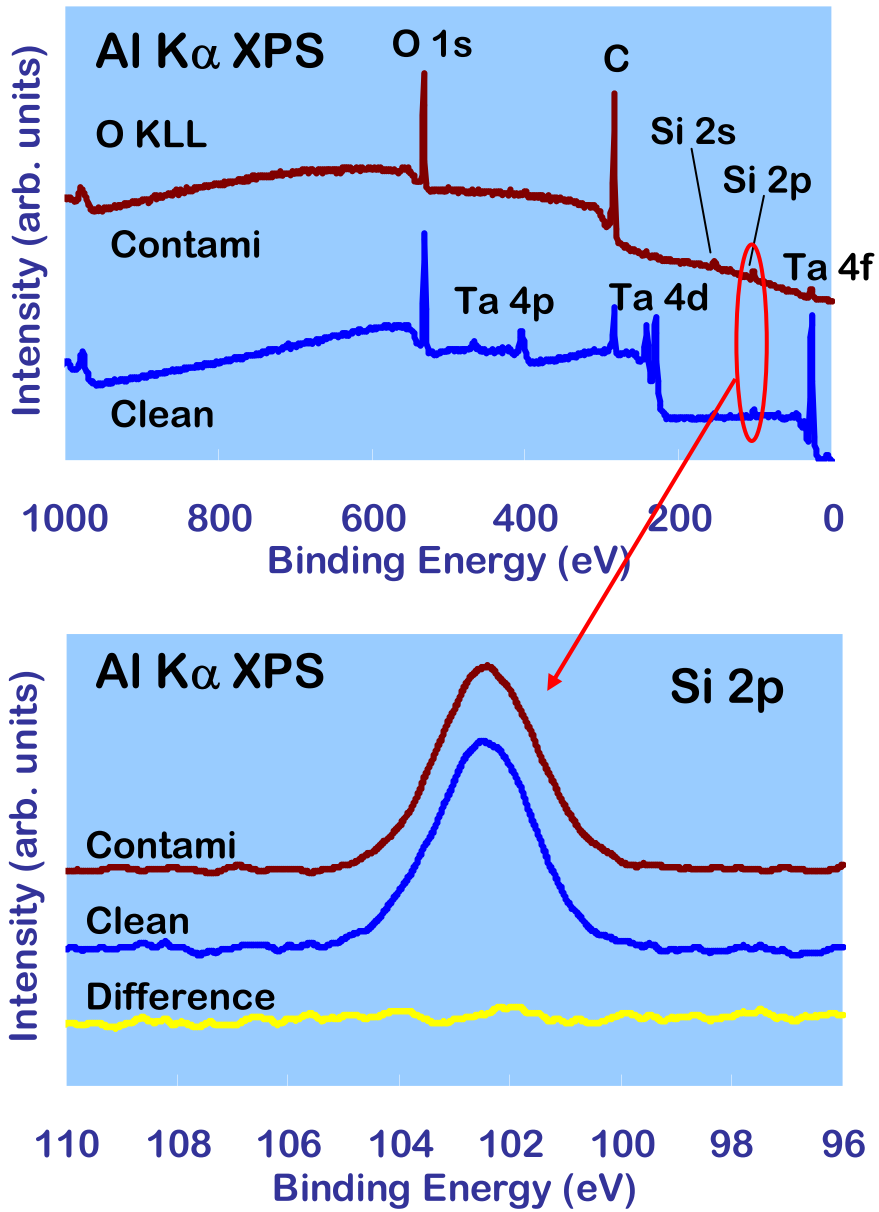
Note that SiO_2 removal process removes not only cleaning residue but also natural oxide of Si capping then mutiple application will damage the multilayer.



Favorable Solution

Contamination of EUV1

- It seems no Si is contained in a contamination on a mask of EUV1.
- For such contamination, both of H radical and pure O_3 can be applied without wet SiO_2 removal.
- It's important to operate in such vacuum conditions.



Conclusion

	C	C w/Si	SiO_2	Si-cap	Ru-cap
H	☺	😐	☹	☺	☺
w/ wet	(needless)	(needless)	☺	😐	(no info)
Pure O_3	☺☺☺	☹	☹	☺	☹
w/ wet	(needless)	☺	☺	😐	☹

☺ = Suitable 😐 = Applicable ☹ = Incompatible

- For Si free contamination on Si-cap, pure O_3 is the best.
- For Si containing contamination, pure O_3 does not work well.
- For SiO_2 containing contamination, H-radical is also no good.
- Residual SiO_2 species can be removed and rescued by wet etching without apparent damege.
- Si free vacuum condition is essential.

Summary

- Origin of Si contained in carboneous contamination is investigated.
- Cleanability of pure O_3 and H-radical cleaning, and behaviour of Si while cleaning is examined.
- Rescue process for degradation by residual SiO_2 is demonstrated.
- In some case, contamination contains little Si. It's important to operate in such a vacuum conditions.

Acknowledgment

SR contamination samples are prepared by H. Ikeda at SR center of Ritsumeikan University.

This work was supported by New Energy and Indastrial Technology Development Organization.